COMMONWEALTH OF AUSTRALIA

Patents Act

COMPLETE SPECIFICATION

(ORIGINAL)

Class Int. Class

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Patents Act 1952 the Commissioner directs that this application be open for inspection by the public under Section 41 of the Act
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49659

APPLICANT'S REF.: 17002-F

Name(s) of Applicant(s): THE DO CHEMICAL COMPANY

Address(es) of Applicant(s): 2030 Abbott Road, Midland, Michigan, United States of America.

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APPLICATION ACCEPTED
26 APR 1979
PATENT OFFICE

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~~37-41~~ Queen Street
Melbourne, Australia, 3000

Complete Specification for the invention entitled:

"DEHYDROGENATION OF ALKYL AROMATIC HYDROCARBONS"

The following statement is a full description of this invention, including the best method of performing it known to applicant(s):

BNSDOCID: <AU___499659B2_I_>

499659

(Non-convention).
(DECLARATION)

Commonwealth of Australia

Patents Act 1952-1969

DECLARATION IN SUPPORT OF AN APPLICATION FOR A PATENT

(1) Insert Full Name of Applicant(s).

In support of the Application made by(1) THE DOW CHEMICAL COMPANY, a corporation organized and existing under the laws of the State of Delaware, and having an office and place of business at Midland, County of Midland, State of Michigan, United States of America,

(2) Insert Title of Invention.

for a patent for an invention entitled(2) "DEHYDROGENATION OF ALKYL AROMATIC HYDROCARBONS"

(3 Insert Full Name and Office of Declarant.

I, (3) WILLIAM MILLER YATES, General Patent Counsel 84260/75

(4) Insert Address of Declarant.

of(4) THE DOW CHEMICAL COMPANY, Midland, Michigan, United States of America,

do solemnly and sincerely declare as follows:—

(5) Insert Full Name of Applicant Company.

1. I am authorized by(5) THE DOW CHEMICAL COMPANY

the applicant for the patent to make this declaration on its behalf.

(6) Insert Full Name of Inventor(s)

2.(6) FREDERICK JOHN SODERQUIST, 817 Harding Road, Essexville, County of Bay, State of Michigan, United States of America; THEODORE THADDEUS

(7) Insert Full Address of Inventor(s).

of(7) WAZBINSKI, 201 Main Street, Bay City, County of Bay, State of Michigan, United States of America; NATHAN WALDMAN, 2105 Bayliss, Midland, County of Midland, State of Michigan, United States of America

are the actual inventor(s) of the invention and the facts upon which the applicant company is entitled to make the application are as follows:—

(8) Specify legal relationship between Applicant Company and Inventor(s). (See above.)

The applicant Company is the assignee of the said invention from the said actual inventor(s).

Declared at Midland, Michigan, U.S.A. this 22 day of August 1975

CORP. SEAL

26 AUG 1975

THE DOW CHEMICAL COMPANY

To THE COMMISSIONER OF PATENTS.

By _____ (Signature of Declarant.)

Official File 63/123

WILLIAM MILLER YATES
General Patent Counsel

BNSDOCID: <AU____499659B2_I_>

(Non-convention)

Commonwealth of Australia

(DECLARATION)

Patents Act 1952-1969

DECLARATION IN SUPPORT OF AN APPLICATION FOR A PATENT

(1) Insert Full Name of Applicant(s).

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(2) Insert Title of Invention.

for a patent for an invention entitled(2) "DEHYDROGENATION OF ALKYL AROMATIC HYDROCARBONS"

(3 Insert Full Name and Office of Declarant.

I, (3) WILLIAM MILLER YATES
General Patent Counsel

84260/75

(4) Insert Address of Declarant.

of(4) THE DOW CHEMICAL COMPANY, Midland, Michigan, United States of America,

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1. I am authorized by(5) THE DOW CHEMICAL COMPANY

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(8) Specify legal relationship between Applicant Company and Inventor(s). (See above.)

(8) The applicant Company is the assignee of the said invention from the said actual inventor(s).

Declared at Midland, Michigan, U.S.A. this 12 day of August 1975

CORP. SEAL

26 AUG 1975

THE DOW CHEMICAL COMPANY

SIGNATURE

By W M Yates

To: THE COMMISSIONER OF PATENTS.

(Signature of Declarant.)

Official File 63/123

WILLIAM MILLER YATES
General Patent Counsel

BNSDOCID: <AU____499659B2_I_>

The present invention is a method for activating self-regenerative dehydrogenation catalysts used in dehydrogenating alkyl aromatic hydrocarbons.

Dehydrogenation of alkyl aromatic hydrocarbons, such as ethyl benzene to styrene, ethyl toluene to vinyl toluene, diethyl benzene to a mixture of divinyl benzene and vinyl ethyl benzene, isopropyl benzene to isopropenyl benzene, and ethyl naphthalene to vinyl naphthalene, by passing a mixture of steam and such alkyl aromatic hydrocarbon over a "self regenerative" catalyst is known. The "self-regenerative" catalysts are usually described as those containing one or more oxides of iron, zinc, chromium or magnesium, as the major ingredient, and an alkali metal oxide, hydroxide or carbonate, particularly potassium or rubidium oxides, hydroxides or carbonates, as water gas reaction-promoting ingredients. This reaction tends to mitigate carbon build-up on the catalyst surface, thereby permitting long periods of continuous dehydrogenation cycles for converting alkyl aromatic hydrocarbons having at least one alkyl group of 2 to 3 C atoms to the corresponding alkenyl aromatic hydrocarbon. Representative "self-regenerative" catalysts are disclosed in U.S. Patents 2,370,797, issued to Kearby, March 6, 1945, 2,414,585, issued to Eggertsen et al., January 21, 1945, 3,703,593, issued to Turley et al., November 21, 1972, and 3,205,179, issued to Soderquist et al., September 7, 1965. These catalysts usually contain one or more of the oxides of iron, zinc, chromium or magnesium as the major ingredient and an alkali metal oxide, hydroxide or carbonate, preferably the potassium compound, as a water gas-promoting

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ingredient. The catalysts may also contain other additives such as stabilizers, binders and porosity control agents. These additives are known in the art and are described in the above cited patents.

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It has been found that a self-regenerative catalyst which consists essentially of a major proportion of at least one oxide of iron, zinc, chromium or magnesium, and which also contains an amount of an alkali metal oxide, hydroxide, or carbonate, preferably the potassium compounds, to promote the water gas reaction, a chromium compound as a promoter, and optionally, a stabilizer, binders and/or porosity control agents, can be activated by short, periodic steaming cycles (without presence of alkyl aromatic hydrocarbon).

The present invention is a method of activating self-regenerative dehydrogenation catalysts used for dehydrogenating alkyl aromatic hydrocarbons having from 1 to 2 six-membered rings and from 1 to 2 alkyl groups of 2-3 carbon atoms to the corresponding alkenyl aromatic hydrocarbon, by passing a mixture of steam and said alkyl aromatic hydrocarbon ~~over said catalyst at a temperature of 600-700°C., said method~~ comprising interrupting the feed of said alkyl aromatic hydrocarbon and continuing the feed of steam at said temperature range for a period of 7-30 minutes each 24-48 hours; resuming the feed of said alkyl aromatic hydrocarbon under high severity reaction conditions; and repeating said activation cycles and said alkyl aromatic hydrocarbon dehydrogenation cycles.

The steaming cycle of about 7-30 minutes every 24-48 hours at a temperature of from about 600° to about ~~700°C., is sufficient to activate the catalysts. Most~~

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over said catalyst at a temperature of 600-700°C., the steam/hydrocarbon ratio being in the range of 0.4 to 1 to 6 to 1 said method comprising interrupting the feed of said alkyl aromatic hydrocarbon and continuing the feed of steam at said temperature range for a period of 7-30 minutes each 24-48 hours; resuming the feed of said alkyl aromatic hydrocarbon under high severity reaction conditions; and repeating said activation cycles and said alkyl aromatic hydrocarbon dehydrogenation cycles.

The steaming cycle of about 7-30 minutes every 24-48 hours at a temperature of from about 600° to about 700°C., is sufficient to activate the catalysts. Most

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conveniently the previous operating temperature is used for activation.

Activation of the catalyst apparently is not due to decoking, because little or no carbon oxides are found in the effluent during the activation cycle.

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After activation, the conversion of alkyl aromatic hydrocarbons to alkenyl derivatives is increased, the selectivity remains high and the dehydrogenation cycle can be run under high severity conditions, e.g. low steam to hydrocarbon weight ratios or higher temperatures, or both, without excessive coking of the catalyst. It is thus possible to attain increased throughput per reactor and also to obtain higher yields of alkenyl aromatic hydrocarbon at lower reaction temperatures.

The catalytic dehydrogenation of alkyl aromatic hydrocarbon having at least one alkyl group with 2 to 3 C atoms is known to be an equilibrium reaction. It is also known that as the hydrogen partial pressure in the dehydrogenation step is decreased, the ratio of styrene to ethyl benzene is increased at any given temperature. Similarly, an increase in temperature at any given partial pressure of hydrogen, also results in an increase in the styrene/ethyl benzene ratio. It is also known that as temperature increases coking is also increased at any given space velocity, and that if space velocity is reduced (reaction time increased) at any given temperature, the degree of coking increases.

In addition, the activity of the particular catalyst must be taken into consideration. An overactive catalyst tends to convert a high percentage of the alkyl benzene, but its specificity to simple dehyrogenation to alkenyl benzenes is comparatively low.

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In commercial single-stage adiabatic reactors the available self-regenerative catalyst have functioned satisfactorily at comparatively high steam to alkyl aromatic hydrocarbon ratios and at conversions of about 38% or slightly higher. The steam ratio will vary somewhat depending on the particular alkyl aromatic hydrocarbon undergoing dehydrogenation.

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Representative alkyl aromatic hydrocarbons and ranges of steam to hydrocarbon ratios of the processes of the prior art are tabulated below.

TABLE I

Hydrocarbon	Steam/Hydrocarbon Ratio
Ethylbenzene	2.6 to 1 to 2.0 to 1
Ethyltoluene	5 to 1 to 3 to 1
Diethylbenzene	8 to 1 to 3 to 1
Isopropylbenzene	3 to 1 to 2 to 1

When the catalysts are activated by steaming for 7 to 30 minutes ever 24-48 hours, the ratios are as follows.

TABLE II

Hydrocarbon	Steam/Hydrocarbon Ratio
Ethylbenzene	1 to 1 to 0.4 to 1
Ethyltoluene	3 to 1 to 1.5 to 1
Diethylbenzene	6 to 1 to 1.5 to 1
Isopropylbenzene	1.5 to 1 to 0.4 to 1
Ethyl naphthalene	1.5 to 1 to .4 to 1
Ethyl biphenyl	2 to 1 to .8 to 1

~~Usually, the~~ The effect of the above defined steam activation of catalyst is not apparent if the steam-hydrocarbon ratios are increased appreciably above the maximum values given in Table 2.

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Although all the self-regenerative catalysts tested have responded to the activation procedure, the degree of response is not uniform for each such catalyst. In general, the greatest degree of desirable activation was found with catalysts containing approximately equal amounts by weight of ferric and zinc oxides containing from about 5 to about 30% by weight of potassium oxide, hydroxide or carbonate, from about 5 to about 10 weight percent of a copper, cadmium, thorium or silver oxides, from about 5 to 10 weight percent of alkali metal chromate, a minor amount 1 to 5 percent of a refractory type cement, and a minor amount of carbonaceous material such as methyl cellulose ethers, graphite or other ingredients defined in U.S. Patent 3,205,179, previously identified.

A representative catalyst made by the procedure of U.S. Patent 3,205,179 contained the following.

Ingredient	Weight Percent
Fe_2O_3	24.81 - 30.0
ZnO	24.81 - 30.0
K_2CO_3	9 - 22.5
Cu_2O	7.44 - 9.0
$Na_2Cr_2O_7$	7.44 - 9.0
Alumina (low silica) Cement	3.90
Methyl Cellulose	4.00
Graphite	5.10

Other catalysts which are especially responsive to the activation procedure are those which are made from a mixture of hydrated (yellow) iron oxide and anhydrous (red) iron oxide in a weight ratio of 1:4 to 17:20 and about 13:7 to 4:1, respectively. These catalysts and their

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methods of preparation are described in U.S. Patent 3,703,593, previously identified. A representative catalyst had the following composition. Fe_2O_3 + $Fe_2O_3 \cdot H_2O$ 58.9%, K_2CO_3 16.7%, $K_2Cr_2O_7$ 2.5%, V_2O_5 2.5%, methyl cellulose 8.3%, graphite 8.3%, cement 2.8%.

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Other catalysts which are activated so that they perform better under high severity reaction conditions (e.g. low steam:hydrocarbon ratio or high temperature or both) include those having the following compositions.

	Weight Percent				
Component	I	II	III	IV	V
Fe_2O_3	74.5	83.0	87.9	71.9	62.5
Cr_2O_3	2.0	2.2	2.5	2.3	2.2
K_2O	-	-	9.6	-	-
K_2CO_3	20.0	14.8	-	25.8	35.3
V_2O_5	3.5	-	-	-	-

The steam to hydrocarbon ratio during the dehydrogenation cycle is within the ranges defined in Table 2 above.

All the tests reported below were run in a stainless steel tubular reactor 36 inches (0.914 m.) long, with an I.D. of 824 inches (2.2 cm.). The reactor was electrically heated and was equipped with metered steam and hydrocarbon feed systems, temperature controls and recovery apparatus. In each instance the reactor was loaded with 70 ml. of catalyst pellets.

Conversion is the percentage of the original alkyl aromatic hydrocarbon converted to the alkenyl aromatic derivative per pass. Selectivity is the percentage of the consumed alkyl aromatic hydrocarbon that resulted in the formation of a desired alkenyl aromatic derivative per pass.

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Example 1

The alkyl aromatic compound used was ethyl toluene. The steam to hydrocarbon weight ratio was 1.7 to 1. The catalyst contained 24.81 weight percent Fe_2O_3, 24.81 ZnO, 22.50% K_2CO_3, 7.44% Cu_2O, 7.44% $Na_2Cr_2O_7$, 3.90 alumina cement, 4.00% methyl cellulose and 5.10% graphite, before calcining. The mixture was formed into a paste with water, extruded, pelletized and dried at 110°C. The catalyst was thereafter steamed at 200 to 600°C. for 3 hours and then roasted for 6 hours at 810-845°C.

Reaction conditions were adjusted to obtain a steady state of about 40% conversion of the ethyl toluene. The temperatures ranged between 638 and 645°C. At 642°C. the conversion was 40.6 with a selectivity to vinyl toluene of 91.7%. The catalyst was then steamed for 15 minutes at 642°C. and, thereafter the ethyl toluene feed was resumed. The reaction temperature was maintained at 640-645°C. A steaming cycle of about 15 minutes duration every 24 hours (ethyl toluene feed was cut off) was provided to activate the catalyst. Samples were taken for analysis about 1/2 hour before steaming and about 1 1/2 hours after steaming. Data taken during the test are given below.

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Days	Temp. °C.	% Conv.	% Selectivity
1	642	41.0	92.3
2	645	40.3	91.9
3	645	42.1	92.9
4	640	39.4	91.9
6	640	39.6	91.8
7	643	40.6	91.7
8	638	38.8	92.2
9	642	40.6	91.7
Steam Cycle			
9	642	47.7	91.5
10	642	46.9	91.7
Steam Cycle			
10	642	48.3	91.9
11	640	46.7	91.9
Steam Cycle			
11	640	48.4	92.3
13	640	46.8	92.0
Steam Cycle			
13	642	48.9	92.1
14	645	47.6	91.8
Steam Cycle			
14	645	49.7	92.0
15	643	47.7	91.9
Steam Cycle			
15	643	50.0	91.4
16	642	47.7	91.8
Steam Cycle			
16	642	50.1	92.0
17	642	48.8	91.9
Steam Cycle			
17	642	50.1	92.0

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For comparative purposes a non self-regenerative catalyst having all the ingredients above in the same proportions, except that K_2CO_3 was omitted, was tested. The catalyst was steamed for 15 minutes every 24 hours at the reaction temperature. The steam to ethyl toluene ratio was 1.7 to 1. Data taken during this test are given below.

Days	Temp °C.	% Conv.	% Selectivity
2	687	44.0	84.1
3	690	41.9	83.8
4	686	39.3	84.3
8	681	36.4	84.1
9	694	40.3	82.5
Steam Cycle			
9	696	40.6	81.8
Steam Cycle			
10	694	42.2	82.3
Steam Cycle			
10	693	39.3	81.6
Steam Cycle			
11	693	39.5	81.9
Steam Cycle			
11	695	39.8	81.3

From the above it is apparent that the steaming cycle had no benefit for this catalyst.

In another series of runs, the self-regenerative catalyst described above in this example was tested at a steam to ethyl toluene ratio of 3 weight parts to 1. The temperature for 40% conversion was 621°C. Thereafter the temperature was maintained at 620-626°C. and a 15 minute steaming cycle was given to the catalyst each 24 hour period. During these tests the following data were taken.

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		Temp. °C	% Conv.	% Selectivity
7	B	626		
	A	625	44.9	94.0
8	B	623	42.2	93.4
	A	623	42.7	94.0
9	B	620	40.9	93.8
	A	621	42.4	93.9
10	B	622	41.4	93.9
	A	623	42.4	93.9
11	B	623	41.8	93.5
	A	623	43.4	93.8
12	B	624	42.4	93.8
	A	624	43.7	93.7
13	B	623	42.6	93.9
	A	623	43.8	93.5
14	B	625	43.1	93.3
	A	625	43.1	93.6
15	B	624	43.1	93.3
	A	624	44.6	93.5

A - After steaming of catalyst

B - Before steaming

The data show that the conversion increase is perceptible but is considerably lower than that at a 1.7 to 1 steam to hydrocarbon ratio.

Example 2

In a series of tests using the self-regenerative catalyst of Example 1 the degradation pattern of the catalyst activity after a 15 minute steaming cycle was compared with a pattern after a 1 hour steaming cycle. It was found that a 1 hour cycle does not improve catalyst activity to any greater degree than the 15 minute cycle.

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Using the same steam-ethyl toluene ratio and a 24 hour steaming cycle showed substantially no greater increase in conversion to vinyl toluene than the 15 minute cycle and selectivity had decreased slightly. A 24 hour steaming cycle, however, increases the negative effect of by-product formation.

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Example 3

In this series, the catalyst was brought to steady state of about 40% conversion, using a steam-ethyl toluene ratio of 1.7 to 1. The temperature was 641-648°C. Thereafter the catalyst was subjected to 15 minute steaming cycle each 24 hours for 21 days and then to 7 minute steaming cycles each 24 hours for 8 days. It was found that a 40% conversion level could be maintained at temperatures considerably lower than 640°C. and about a 2% higher selectivity was realized. Data taken during these tests are tabulated below.

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Days	Temp. °C.	% Conv.	% Selectivity
6	648	39.9	91.0
7	646	39.2	91.8
11	641	38.8	92.0
12	643	39.3	92.0
13	647	41.3	92.0
14	647	41.7	91.8
17	642	37.[illegible]	92.1
Steam Cycle (15 min.)			
18	629	43.1	93.7
Steam Cycle			
19	628	43.1	94.0
Steam Cycle			
20	623	39.8	94.2
Steam Cycle			
21	622	38.9	94.8
Steam Cycle			
24	621	36.9	94.6
Steam Cycle			
25	629	42.2	93.6
Steam Cycle			
27	630	42.2	94.4
Steam Cycle			
28	625	38.7	94.1
Steam Cycle			
31	626	40.5	94.3
Steam Cycle			
32	627	40.8	94.2
Steam Cycle			
33	627	40.9	93.4
Steam Cycle			
34	628	40.7	93.9
Steam Cycle			
35	628	41.6	94.3
Steam Cycle			
38	627	39.5	94.3
Steam Cycle			
39	625	39.7	94.4

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Days	Temp. °C.	% Conv.	% Selectivity
Steam Cycle			
40	627	42.3	93.6
41	626	41.1	93.8
Steam Cycle (7 min.)			
43	628	42.7	93.6
Steam Cycle			
44	628	42.	94.3
Steam Cycle			
45	628	41.9	94.2
Steam Cycle			
46	628	42.1	93.9
Steam Cycle			
47	628	42.2	94.1
Steam Cycle			
48	626	40.9	94.4
Steam Cycle			
49	628	41.0	94.1

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Example 4

Ethyl benzene was dehydrogenated to styrene by the procedure described in Example 1 using a catalyst containing 87.9 weight percent Fe_2O_3, 2.5% Cr_2O_3, and 9.6% K_2O. When a steam to hydrocarbon ratio of 1 to 1 or lower was fed to the reactor at temperature of 590 to about 600°C., with 15 minute steaming cycles each 24 hours, there was a perceptible change in conversion but no change if steam-ethyl benzene ratios greater than 1 to 1 were used. However, when the severity was increased by lowering the steam to ethyl benzene ratio to 0.7 to 1 or as low as 0.4 to 1 and temperature was increased considerably, the activation effect

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of 15 minute steaming cycles each hours was readily apparent. Tabulated below are data taken at 0.7 and 0.4 parts of steam per part of hydrocarbon.

Steam - Ethyl Benzene Ratio 0.7 to 1

Days	Temp. °C.	% Conv.	% Selectivity
36	628	37.2	89.6
Steam Cycle			
36	628	40.0	91.4
37	631	38.5	92.0
Steam Cycle			
37	630	42.7	91.6
39	629	38.1	90.9
Steam Cycle			
39	630	42.6	90.3
40	629	39.1	91.6
Steam Cycle			
40	630	44.9	91.1
41	631	38.7	90.7
Steam Cycle			
41	632	47.0	91.0
42	630	39.1	91.1
Steam Cycle			
42	631	46.4	90.3
43	631	39.4	90.7
Steam Cycle			
43	629	43.6	91.2
44	631	40.2	-
Steam Cycle			
44	631	45.4	-
45	628	39.6	-

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Days	Temp. °C.	% Conv.	% Selectivity
Steam Cycle			
45	628	45.4	-
46	627	38.3	91.0
Steam Cycle			
46	627	41.6	-
47	627	38.5	-
Steam Cycle			
47	626	46.8	-

Steam - Ethyl Benzene Ratio 0.4 to 1

Days	Temp. °C.	% Conv.	% Selectivity
6	680	30.3	75.7
Steam Cycle			
6	681	38.0	79.9
7	682	30.6	75.9
Steam Cycle			
7	682	38.6	79.9
11	681	35.1	77.2
Steam Cycle			
11	681	40.1	80.7
12	681	33.8	77.8
Steam Cycle			
12	681	45.9	82.1
13	681	33.7	78.3
Steam Cycle			
13	681	43.7	82.1
14	681	33.1	78.0
Steam Cycle			
14	681	45.9	83.5
15	682	32.8	78.3

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Cont.

Days	Temp. C.	% Conv.	% Selectivity
Steam Cycle			
15	682	43.8	83.0
17	680	36.7	79.6
Steam Cycle			
17	680	46.9	83.3
18	680	34.7	77.8
Steam Cycle			
18	681	43.7	80.4

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Similar results are obtained with a catalyst analyzing 74.5 weight percent Fe_2O_3, 2.0% Cr_2O_3, 20.0% K_2CO_3, and 3.5% V_2O_5. Tests were run with this catalyst to determine whether excess coking of catalyst at the end of a 24 hour period at 630°C. and a steam to ethyl benzene ratio of 1 to 1 caused the lower activity. During a 15 minute steam cycle the noncondensible vent gases were collected and analyzed. The carbon content of the catalyst ranged from 2.2 to 2.5 weight percent. This compares with a typical range of 2.4 to 2.6% carbon on a catalyst during low severity operations e.g. 3 to 1 steam to ethyl benzene ratio and a temperature of about 590°C. These tests show excessive coking is not the cause of lowering catalyst activity.

Example 5

Isopropyl benzene was dehydrogenated to alpha methyl styrene with the catalyst described in Example 1. The procedure used was similar to that described above, in that, after attaining about 40% conversion, the steaming cycle of about 15 minutes each 24 hours was begun. Data taken during the tests are tabulated below.

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Steam - I ropyl Benzene Ratio 1 t 1

Days	Temp. °C.	% Conv.	% Selectivity
32	620	41.6	96.6
Steam Cycle			
32	619	51.8	97.4
33	619	40.2	97.4
Steam Cycle			
33	619	51.8	97.4
34	621	40.6	96.2
Steam Cycle			
34	621	56.0	97.7
35	621	39.5	97.4
Steam Cycle			
35	621	51.4	98.0
38	625	42.0	96.0
Steam Cycle			
38	623	57.5	97.4
39	623	42.9	95.3
Steam Cycle			
39	620	58.1	97.5
40	620	40.2	95.9
Steam Cycle			
40	619	59.7	97.5
41	624	40.4	95.8
Steam Cycle			
41	625	59.9	97.3
45	622	38.5	95.5
Steam Cycle			
45	619	54.0	97.5
46	618	37.3	96.0

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Days	Temp. C.	% Conv.	% Selectivity
Steam Cycle			
46	618	43.9	96.9
47	617	35.7	96.6
Steam Cycle			
47	622	45.6	98.6

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When tests were run at a steam to isopropyl benzene ration of 2 to 1 at 586-596°C., the activation of catalyst was perceptible, but not of the magnitude shown at the 1 to 1 ratio.

Example 6

The catalyst described in Example 4 was used to dehydrogenate diethyl benzene (DEB). A mixture of ethyl vinyl benzene (EVB) and divinyl benzene (DVB) was produced. At a steam to hydrocarbon ratio of 6 to 1 the improvement in catalyst activity is perceptible, but not as great as that obtained at a ratio of 3 to 1. Tabulated below are data obtained while dehydrogenating diethyl benzene at a steam to hydrocarbon ratio of 3 to 1. The steam cycle was of 15 minutes duration each 24 hours.

Temp. °C.		Crude Product Anal. % DEB.	% EVB.	% DVB.	EVB. + DVB.
645	B	44.1	26.3	23.3	49.6
645	A	35.6	28.1	28.1	56.2
645	B	46.5	24.7	22.9	47.6
644	A	36.0	27.6	28.1	55.7
644	B	44.8	26.7	22.8	49.5
644	A	36.2	27.7	27.5	55.2
644	B	45.7	26.2	22.1	48.3

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Cont.

Temp. C.		Crude Product Anal. % DEB.	% EVB.	% DVB.	EVB. + DVB.
643	A	36.2	27.4	27.2	54.6
644	B	45.3	26.6	22.5	49.1
643	A	36.0	27.9	29.5	57.4

A - after steaming

B - before steaming

These data show that the major increase was in the amount of divinyl benzene produced.

The conversion of ethyl naphthalene to vinyl naphthalene or ethyl biphenyl to vinyl biphenyl can be effected with the self-regenerative catalysts recited above. The dehydrogenation of the alkyl bicyclic compounds takes place under about the same conditions as those used for dehydrogenating the alkyl monocyclic hydrocarbons with comparable conversions and selectivities for the dehydrogenation of ethyl naphthalene. However, when ethyl biphenyl is the hydrocarbon undergoing dehydrogenation, the conversion and selectivity is generally slightly lower than those for ethyl naphthalene at identical operating conditions.

All the runs above were made at a luqiud hourly space velocity of about 0.5. However, the space velocity can range from about 0.1 to about 1. In a large scale test for converting ethyl toluene to vinyl toluene a 3 to 1 steam to ethyl toluene, a liquid hourly space velocity of 0.3 and a temperature of 620-640°C., with 15 minute steaming cycles each 24 hours, was found to improve conversions and selectivities of about the same magnitude as shown in the examples.

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The process of this invention is applicable to adiabatic or heated case reactor procedures. The catalyst can be a fixed bed, either radial or packed, or a fluidized bed. In addition, the process is applicable to single or multi reactor systems, especially those multi reactor systems in which interstage steam injection is possible, although multi reactor systems with provision for indirect heat exchange between stages is also operable.

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The claims defining the invention are as follows:-

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1. A method of activating self-regenerative dehydrogenation catalysts used for dehydrogenating alkyl aromatic hydrocarbons having from 1 to 2 six-membered rings and from 1 to 2 alkyl groups of 2-3 carbon atoms to the corresponding alkenyl aromatic hydrocarbon, by passing a mixture of steam and said alkyl aromatic hydrocarbon over said catalyst at a temperature of 600-700°C., the steam/hydrocarbon ratio being in the range of 0.4 to 1 to 6 to 1 said method comprising interrupting the feed of said alkyl aromatic hydrocarbon and continuing the feed of steam at said temperature range for a period of 7-30 minutes each 24-48 hours; resuming the feed of said alkyl aromatic hydrocarbon under high severity reaction conditions; and repeating said activation cycles and said alkyl aromatic hydrocarbon dehydrogenation cycles.

2. A method according to Claim 1 in which the catalyst has a weight ratio of hydrated iron oxide and anhydrous iron oxide of 1:4 to 17:20 and 13:7 to 4:1, respectively.

3. A method according to Claim 1 in which the catalyst contains from 62.5 to 87.9% by weight of Fe_2O_3, from 2 to 2.5% by weight of Cr_2O_3, and from 9.6 to 35.3% by weight of K_2O or K_2CO_3.

4. A method according to Claim 3 in which the catalyst contains about 3.5% by weight of V_2O_5.

5. A method according to Claim 1 in which the catalyst contains from 24.8 to 30% by weight each of Fe_2O_3 and ZnO, from 5 to 30% by weight of potassium oxide, hydroxide or carbonate, from 5 to 10% by weight of an oxide

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of copper, cadmium, thorium or silver, from 5 to 10% by weight of an alkali metal chromate, from 1 to 5% by weight of a refractory cement and a small amount of a carbonaceous material.

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6. A method according to any one of the preceding claims in which the alkyl aromatic hydrocarbon is ethyl toluene, and the feed during dehydrogenation contains from 1.5 to 3 parts by weight of steam per part of said hydrocarbon.

7. A method according to any one of the preceding claims in which the steam to hydrocarbon ratio is 1.7 to

8. A method according to any one of claims 1 to 5 in which the alkyl aromatic hydrocarbon is ethyl benzene and feed during dehydrogenation contains from 0.4 to 1 part of steam per part of hydrocarbon.

9. A method according to any one of claims 1 to 5 in which the alkyl aromatic hydrocarbon is diethyl benzene and the feed during dehydrogenation contains from 1.5 to 6 parts of steam per part of hydrocarbon.

10. A method according to any one of claims 1 to 5 in which the alkyl aromatic hydrocarbon is isopropyl benzene and the feed during the dehydrogenation step contains 0.4 to 1.5 parts of steam per part of hydrocarbon.

11. A method according to any one of claims 1 to 5 in which the alkyl aromatic hydrocarbon is ethyl biphenyl and the feed during the dehydrogenation step contains from 0.8 to 2 parts of steam per part of hydrocarbon.

12. A method according to claim 1 substantially as hereinbefore described with reference to any one of the Examples.

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13. Self-regenerative dehydrogenation catalysts whenever activated by a method according to any one of the preceding claims.

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